253

# TRANSFORMATION OF CLAY MINERALS BY CALCIUM HYDROXIDE ATTACK

OCTOBER, 1963

NO. 31

by

S. DIAMOND
J.L. WHITE
and
W.L. DOLCH

Joint Highway Research Project

PURDUE UNIVERSITY
LAFAYETTE INDIANA

Technical Paper

# TRANSFORMATION OF CLAY MINERALS BY CALCIUM HYDROXIDE ATTACK

TO: K. B. Woods, Director
Joint Highway Research Project

October 31, 1963

FROM: H. L. Michael, Associate Director
Joint Highway Research Project

Project: C-36-47I
File: 4-6-9

Attached is a Technical Paper entitled "Transformation of Clay Minerals by Calcium Hydroxide Attack" which has been authored by Messrs. Sidney Diamond, Joe L. White and W. L. Dolch. Messrs. Diamond and Dolch are or were members of our staff and the research reported was performed as part of the investigation entitled "Calcium Silicate Hydrates", an HPS financed project.

The paper was presented at the Clay Minerals Conference in Atlanta, Georgia in September 1963 and is proposed for publication in the Proceedings of that Conference. We did not notify the ISHC and the BPR of the presentation before it was presented because we were not aware of the fact that this was required. This error has been called to our attention and we regret that it occurred. Proper credit was given to the ISHC and the BPR in the presentation and Mr. Diamond, a BPR employee in Washington did have a review made of the oral presentation by Bureau officials in Washington before it was presented.

The paper is presented to the Board for approval of the proposed publication. It will be forwarded to the Indiana State Highway Commission and to the Bureau of Public Roads for review and also for approval of publication.

This is only one of several papers which will be proposed from the referenced research. The other papers will be presented for approval of presentation and publication as soon as they are prepared.

Respectfully submitted,

Harold L. Michael

Harold L. Michael, Secretary

HLM:bc

Attachment

Copy:

F. L. Ashbaucher
J. R. Cooper
W. L. Dolch
W. H. Goetz
F. F. Havey
F. S. Hill
G. A. Leonards
J. F. McLaughlin
R. D. Miles
R. E. Mills
M. B. Scott
J. V. Smythe
E. J. Yoder

Technical

# TRANSFORMATION OF CLAY MINERALS BY

By

Not Released For Publication

Subject to Change

Not Released

Indiana State Highway Commission
or the
Bureau of Public Roads

Lafayette, Indiana

October 31, 1963

# TRANSFORMATION OF CLAY MINERALS BY CALCIUM HYDROXIDE ATTACK

by

SIDNEY DIAMOND [1], JOE L. WHITE, and [illegible]

Purdue University, Lafayette, Indiana

ABSTRACT

Calcium hydroxide was allowed to react with various clays and other silicates at slightly elevated temperatures for several months. The reaction products were examined by x-ray, DTA, and electron microscopy, and were shown to be poorly-crystallized calcium silicate hydrates of the tobermorite family and calcium aluminate hydrate. Quaternary phases were not detected, but some isomorphous substitution probably occurs. The extent of reaction was shown to be such that under appropriate conditions almost all of the clay mineral was decomposed. Electron micrographs of the reacted materials indicated that attack occurred from the edges of the particles, and in general the remaining unattacked portion of the clay did not suffer appreciable loss of crystallinity. It was postulated that the reaction involves progressive dissolution of the mineral at the edges of the particles in the strongly basic environment maintained by the hydroxide solution, followed by separate precipitation of the reaction products.

In these experiments the calcium silicate hydrate generated by the reaction between lime and quartz was uniformly CSH gel; reaction with kaolinite and montmorillonite produced either CSH gel or CSH(I) depending on the conditions of the reaction. At 60°C the

---

1/ Present address: Materials Research Division, Bureau of Public Roads, U. S. Department of Commerce, Washington 25, D. C.

Digitized by the Internet Archive
in 2011 with funding from
LYRASIS members and Sloan Foundation; Indiana Department of Transportation

http://www.archive.org/details/transformationof00diam

alumina-bearing phase was tricalcium aluminate hexahydrate; at lower temperature the phase produced was a hexagonal material closely resembling $4CaO.Al_2O_3.13H_2O$ but retaining a constant 7.6Å basal spacing regardless of its state of wetness or dryness.

It was found that under appropriate conditions the formation of CSH(I) resulted in as effective a cementation as did the formation of CSH(gel).

## INTRODUCTION

Soil engineers have known for many years that treatment of many clay soils with relatively small amounts of calcium hydroxide followed by appropriate compaction and curing produces a highly-cemented material with considerable strength and resistance to the deleterious effects of moisture. The use of lime as a practical soil stabilizing agent is now widespread in the highway construction field, but until recently almost nothing was known of the mechanism of the stabilizing reaction, and little about the nature of the reaction products. Eades and Grim (1960) suggested that the reactions occur in three steps: exchange of calcium ions for those held by the clay, formation of new minerals, and finally the carbonation of any excess lime. The new minerals formed in their experiments were tentatively identified as calcium silicate hydrates resembling tobermorite, but little detailed information was available as to the specific phases formed. Hilt and Davidson (1961) reported the isolation of a reaction product of lime and montmorillonite in comparatively large crystals. Their x-ray study suggested that this product was isostructural with tetracalcium aluminate hydrate, but their analytical results showed that it contained considerably more silica than alumina. More recently

Glenn and Handy (1963) reacted calcium hydroxide and several other varieties of lime with clay minerals; the products reported included a "10 A tobermorite", tetracalcium aluminate hydrates ($\alpha$ and $\beta$ $C_4AH_{13}$) and several other products that they could not conclusively identify.

The designations used by various investigators for the known tobermorite-like calcium silicate hydrate phases are conflicting, but four phases are now generally recognized: tobermorite (a well crystallized mineral readily prepared by hydrothermal means) and three poorly crystallized phases designated by Taylor (1961) as CSH(I), CSH(II), and CSH(gel). The latter phase, which is the cementing agent of portland cement concrete, is also called "tobermorite (G)" (Brunauer and Greenberg, 1962). Recent reviews including information on these phases have been published by Taylor (1961) and by Brunauer and Greenberg (1962).

In contrast to most of these calcium silicate hydrates, the calcium aluminate hydrates are generally well-crystallized. Proper names are not available for most of the phases, the materials usually being referred to by an abbreviated compositional notation; that is the particular oxide composition of a phase is expressed by the first letter of the name of the metal and an appropriate subscript denoting the number of moles present. Thus, the compound tricalcium aluminate hexahydrate is referred to as $C_3AH_6$, etc. $C_3AH_6$, a cubic phase, is readily identified by its characteristic x-ray powder pattern. A number of hexagonal and psuedohexagonal phases also occur, mostly based on the compositions $C_4AH_{13}$ and $C_2AH_8$. Identification of these phases is complicated by the existence of polymorphic varieties, by

the general similarity of powder patterns of different members of the group, by the frequent occurrence of stacking variations that cause small differences in the powder patterns of different specimens of the same material, by the occurrence of solid solution between the end members, by the likelihood of isomorphous replacement involving $CO_3$, Si, and other ions, and by the ready transformation of some of these phases into others. A useful review of this complex subject has been given by Jones (1962).

Acknowledgments

The present work is part of a larger study the results of which were presented in a Ph. D. thesis submitted to the faculty of Purdue University (Diamond, 1963). In addition to the present work, intensive studies were performed on tobermorite and on the several CSH phases, the results of which will be published elsewhere.

The research was carried out in the laboratories of the Agronomy Department and of the Joint Highway Research Project, Purdue University. Financial support by the Indiana State Highway Department and by the Bureau of Public Roads, U. S. Department of Commerse, is gratefully acknowledged. Thanks are due to Dr. John Radavich of Micromet Laboratories, Inc., who performed the electron microscopy, and to John Allen and Joanne Johannsen who assisted in a number of the procedures.

## EXPERIMENTAL

### Materials

Reactions of calcium hydroxide with clays and other silicates were carried out under three sets of experimental conditions, involving, respectively, compacted solid mixtures, slurries, and dilute suspensions. In each instance freshly-opened Mallinckrodt AR grade $Ca(OH)_2$ was used.

Experiment 1, in which compacted solid mixtures of the reactants were employed, involved four different silicates as follows:

(a) Quartz - "No. 290 Ground Silica", Ottawa Silica Co. The material passed 270 mesh; essentially all of the small content of clay-sized particles was removed for use in Experiment 2.

(b) Kaolinite - "Hydrite 10" grade, Georgia Kaolin Co.; average particle diameter stated to be 0.5 microns.

(c) Montmorillonite - "Volclay" brand Wyoming bentonite, American Colloid Co., Passing 270 mesh.

(d) Pyrophyllite - Hemp, N. Car., supplied by Ward's Natural Science Establishment. The massive material supplied was carefully ground to pass 270 mesh size, and and the small content of clay size particles was removed for use in Experiment 2.

Examination of these materials for impurities disclosed that the quartz and the kaolinite were essentially pure, that the montmorillonite contained the usual quartz impurities and perhaps others, and that the pyrophyllite contained small amounts of quartz and mica.

Experiment 2, involving mixtures of the reactants in slurry form was carried out with a total of seven materials. Each of these was a relatively pure mineral carefully fractionated by centrifuge methods to contain particles less than 2 microns e.s.d., and subsequently calcium-saturated, washed, dried at 110°C, and powdered. The clays were as follows:

a) Quartz - the clay-size fraction from the Ottawa silica material previously mentioned.

b) Kaolinite - Bath, S. Car. (sample H-5 of the A.P.I. reference collection).

c) Montmorillonite - Otay, Calif. (sample H-24 of the A.P.I. reference collection).

d) Pyrophyllite - Hemp, N. Car. - the clay-size fraction from the pyrophyllite previously mentioned.

e) Illite - Beaver's Bend, Okla. - Reference specimen supplied by the Oklahoma Geological Survey and characterized by Mankin and Dodd (1963).

f) Mica - "Delamica" a delaminated muscovite characterized by White (1956, p. 135).

g) Talc - U.S.P. talc supplied by the Purdue University Pharmacy; origin unknown.

Experiment 3, a reaction carried out with the reactants in dilute suspension, was performed with only a single clay, the Bath kaolinite used in part of Experiment 2.

Reaction Conditions

Experiment 1. -- In the first experiment, 25 g of air-dried silicate material were mixed in the dry state with 10 g of $Ca(OH)_2$. A 20 ml portion of previously-boiled distilled water was then added and the wetted material was thoroughly mixed. After achieving a homogeneous mixture the moist solid material was then compacted by hand into a rigid plastic container. A tight-fitting plastic disc was then pressed into position immediately above the mixture, and about 10 ml of distilled water added above the disc as a $CO_2$ barrier. The lid of the container was then fastened into place and sealed with plastic electrical tape. The sealed containers were then placed in a steam cabinet maintained at approximately 60°C, and allowed to remain without disturbance for 55 days.

Experiment 2 --The second experiment involved the following procedure: A 1 g portion of each $Ca^{++}$ saturated clay-size fraction was mixed with 4 g of $Ca(OH)_2$, and the dry mixture was placed in a 50 ml polyethylene centrifuge tube. The tube was filled with previously-boiled distilled water, closed with a tight-fitting closure, and sealed with plastic electrical tape. After hand shaking to disperse

and mix the resulting slurry, the tubes were mounted horizontally on a reciprocating shaker in such a fashion that the long axes of the tubes were parallel to the direction of motion of the shaker. The shaking apparatus was then mounted inside an air bath regulated at 45°C ( ± 1°). The shaker was programmed to operate continuously except for a 90 minute rest period every eight hours, and this regime was maintained for a period of 60 days.

Experiment 3. -- In this experiment, 5 g of the fractionated $Ca^{++}$ saturated Bath kaolinite were mixed with an equal weight of $Ca(OH)_2$, suspended in 150 ml of previously-boiled distilled water, and sealed in a plastic container. The container was mounted near the rim of a 22-inch diameter wooden wheel that was in turn mounted on a shaft so that it could be rotated continuously by a small electric motor. The speed of rotation was regulated at approximately 30 rpm, and the entire apparatus was kept in a constant temperature room at 23°C ( ± 1°). Reaction was allowed to proceed under these conditions for a period of 6 months.

## Methods of Examination of Reacted Mixtures

The products of the several reactions were examined by x-ray diffraction, DTA, and electron microscopic methods, and surface areas were determined for a few of them.

X-ray diffraction.-- A General Electric XRD-5A diffractometer using nickel-filtered Cu K$\alpha$ radiation was employed for x-ray examination. All samples were examined, after drying, by standard random orientation powder-mount techniques. In addition, the reaction products of Experiment 2 were examined in the moist state by mounting the slurry in a sample well of a powder holder that had a number of thicknesses

of filter paper inserted between the frame and the glass slide backing. It was found that this procedure allowed sufficient excess water to be drawn off so that after smoothing the surface the sample would maintain the required geometry on being mounted on the diffractometer. The reaction product of Experiment 3 was examined in the moist state by centrifuging the solids onto the plane face of a porous tile (Kinter and Diamond, 1956).

Differential thermal analysis.-- DTA of the products of Experiment 1 was carried out with a direct-recording apparatus which maintained a constant rate of temperature increase of 10°C per minute. The remainder of the materials were examined (by necessity) with an Eberbach portable DTA unit which requires manual recording of the temperature differentials. The apparatus was modified by replacing the transite thermal insulation unit by a close-fitting sleeve of commercial pipe insulation; this permitted a temperature of 1000°C to be readily attained and resulted in a more nearly uniform temperature increase rate in the higher temperature region. The heating rate attained by this instrument as modified was a linear rate of 58°C per minute from room temperature to approximately 600°C, and subsequently a rate which decreased monotonically to about 5°C per minute at 1000°C. The temperatures of exothermic or endothermic peaks recorded with this instrument are thus not exactly comparable to those obtainable on more nearly standard instrumentation, but checks disclosed that peak shapes are not appreciably distorted.

Electron microscopy.-- Electron microscopic study of the reaction products was carried out with an RCA EMU-3 instrument operated at 50 kvp. Sample preparation was by a non-aqueous dispersion procedure

evolved by Dr. John Radavich of Micro-Met Laboratories, Inc., who prepared the mounts and operated the instrument.

No ultrasonic vibration was required to effect dispersion of the particles, and the danger of artifacts due to violent disruption was avoided. Despite the mildness of the treatment the individual particles are seen to be well-separated from each other and to cover the field uniformly. The clumping together of particles associated with the drying of a drop of a suspension of high surface tension liquid such as water is avoided, and the morphology of the individual particles is clearly visible in most instances.

All of the electron micrographs used in the present study were taken at a direct magnification of 4400x.

Surface area determinations.-- Surface areas were determined for some of the reactants and products by the water vapor adsorption method. Samples were initially dried and outgassed over $P_2O_5$ for four days, then weighed and placed in vacuum desiccators over sulfuric acid solutions at 21°C. After evacuation for at least an hour the samples were permitted to equilibrate for four days, were reweighed, and were then placed over a sulfuric acid solution of a lower concentration, and the procedure was repeated. Five points in the B E T range were secured, and all samples were run in duplicate. The molality of the acid was determined by titration after equilibration, and the partial pressure of water vapor was determined by reference to unpublished data of D. M. Anderson and P. F. Low. The adsorption isotherm was plotted according to the well-known B E T procedure (Brunauer, Emmett, and Teller, 1938), the slopes and intercepts of

the resulting straight lines were determined by least squares, and the parameter "$V_m$" was calculated. Surface areas were calculated from the $V_m$ value using an assigned area per water molecule of $10.3A^2$ for the $Ca(OH)_2$ and $11.4A^2$ for the reaction products (Brunauer and Greenberg 1962).

## EXAMINATION OF REACTION PRODUCTS

### Experiment 1 - Compacted Mixtures at 60°C

Physical appearance and moisture content.-- The wetted lime-silicate mixes were at the start of the experiment plastic except for the quartz. After the reaction the quartz, kaolinite, and montmorillonite mixtures had obviously undergone cementation; they were extremely hard, dry to the touch, and retained their hardness and integrity after several weeks immersion in water. By contrast, the pyrophyllite mixture remained soft and plastic and showed no evidence of cementation.

Some of the reacted material was removed for examination (a hammer and chisel being required) and after powdering, the moisture content was determined by oven drying at 110°. The evaporable moisture content so determined was on the order of 50-60% by weight of solids, very nearly the original moisture content of the mixture. Apparently, only a small portion of the water present had reacted in such fashion as to be held against oven drying, despite the very substantial change in the physical properties of the materials.

X-ray diffraction.-- Diffractometer traces of the quartz, kaolinite, and montmorillonite - lime mixtures before and after reaction are given in Figure 1.

Examination of Figure 1-A reveals that most of the $Ca(OH)_2$ had disappeared during the course of the reaction with quartz, despite

the fact that the intensity of the quartz pattern had not noticeably decreased. Several new peaks attributable to the formation of a poorly-crystalline calcium silicate hydrate are shown. The characteristic peaks for tobermorite-like calcium silicate hydrates occur at about 3.05A, 2.82A, and 1.82A; however, a strong quartz peak at 1.82A interferes with the observation of any new peak at that position.

In Figure 1-B it is apparent that as a result of reaction with kaolinite all of the $Ca(OH)_2$ added to this sample had disappeared. The intensities of the kaolinite lines have been considerably reduced, particularly the (00ℓ) lines. The (001) peak appears to be slightly broadened on the low-angle side, suggesting a slight expansion of some of the layers.

In an attempt to quantify the extent of the reaction the integrated intensity of the kaolinite basal peak at 7.1A was measured for both the starting mixture and the reaction product, measurements being taken in duplicate for each of five separate random orientation powder mounts of each sample. The average integrated intensity for the kaolinite peak in the original reaction mixture was 117 arbitrary units; after reaction it was only 69 arbitrary units, suggesting that perhaps as much as 40% of the kaolinite had been decomposed by the reaction.

A number of new peaks indicative of the formation of crystalline reaction products are reserved in Figure 1-B. Peaks at 3.04A, 2.78A, and 1.79A (not shown) reveal the presence of a poorly-crystallized calcium silicate hydrate; peaks at 5.12A, 3.11A, and an enlargement of the kaolinite peak at 2.28A are attributable to the cubic tricalcium aluminate hexahydrate, $C_3AH_6$.

Figure 1-C reveals that all of the $Ca(OH)_2$ added to the montmorillonite clay reacted. The peaks attributable to residual montmorillonite are lessened in intensity, but the montmorillonite does not appear to have been appreciably disordered. The position of the (060) reflection, not shown in the figure, is unchanged at 1.495A. Reaction has produced broad peaks at 3.06A and at 2.74A, indicative of the formation of a poorly-crystallized calcium silicate hydrate, but no evidence of the $C_3AH_6$ is present. A peak of unknown significance occurs at 9.2A. No crystalline calcium aluminate was observed. This suggests the possibilities of the existence of some of the aluminum in amorphous phases.

Examination of the x-ray diffraction pattern for the pyrophyllite product (not shown) confirms the indication that no appreciable reaction occurred with this material. There is no diminution of the $Ca(OH)_2$ pattern and no evidence of any reaction products having been formed.

Differential thermal analysis.-- DTA diagrams for the four reacted mixtures are given in Figure 2; the heating rate was $10^{\circ}C$ per minute. In general the DTA patterns confirm and supplement the conclusions drawn from the x-ray examination.

The reaction product of quartz and lime has a small endotherm at $510^{\circ}C$, indicative of some unreacted lime. The relative amount may be judged by reference to the corresponding endotherm in the pyrophyllite "product" in which no reaction occurred. The sharp endotherm at $573^{\circ}C$ for the quartz transformation is well marked. The small endotherm at about $760^{\circ}C$ may be due to a trace of carbonation, but it may also be an inherent feature of the calcium silicate hydrate

produced. Synthetic calcium silicate hydrates almost always display this feature. The small but distinct exotherm at 885°C is attributed to the conversion of the dehydrated calcium silicate hydrate to wollastonite.

The DTA pattern for the kaolinite reaction product confirms the complete reaction of all lime. A large number of features are displayed. A similar pattern, lacking only the 200°C endothermic peak, was published by Eades and Grim (1960) for a lime-kaolinite reaction product prepared under somewhat similar conditions. The following tentative explanation is offered for the diagram: it is thought that the 200°C endotherm is due to the dehydration of the calcium silicate hydrate phase; the 370°C endotherm is ascribed to the $C_3AH_6$ phase; the main exotherm at 580°C is residual kaolinite; the peak at 760°C is associated with the calcium silicate hydrate phase, and the final exothermic response probably represents both the kaolinite high-temperature transition and the response incident on the transformation of the dehydrated calcium silicate hydrate phase to wollastonite. The assignment of the 370°C endotherm to $C_3AH_6$ may be questionable, because Majumdar and Roy (1956) reported not one but two endothermic responses for this compound, one at about 320°C and a second, smaller one at about 470°C.

The montmorillonite product yields a DTA diagram that is unusual in that no pronounced endothermic peaks occur. A similar pattern was published by Eades and Grim. A weak dehydration endotherm can be observed at about 160°C; only a faint hint of a residual montmorillonite dehydroxylation endotherm is recorded. There is no endotherm for unreacted lime, nor is there any indication of a calcium aluminate hydrate phase. The strong exotherm at 945°C is at least partially

ascribed to the calcium silicate hydrate phase that almost certainly has incorporated alumina of the decomposed montmorillonite.

The DTA of the pyrophyllite "reaction product" is consistent with the apparent failure of this material to react. The 515°C endotherm is due to unreacted $Ca(OH)_2$, the sharp 573°C peak to a quartz impurity in the pyrophyllite, and the endotherm at 795°C is characteristic of pyrophyllite.

Electron microscopy.-- Typical electron micrographs of the several products are shown in Plate 1. Plate 1-A, the quartz product, consists of elongated fibrous particles that are presumably rolled-up sheets; this is the typical morphology for the CSH(gel) phase as produced in hydrating portland cement. Plates 1-B and 1-C (for the kaolinite and montmorillonite reaction products, respectively) reveal a different morphology. Both these products are largely composed of thin plates or foils, a morphology characteristic of the phase called CSH (I). In addition to these particles Plate 1-B shows a number of small dark particles, some of which have straight edges. These are possibly the $C_3AH_6$ component of the reaction product. The single large particle in the field is a residual kaolinite particle, the edges of which appear to have been frayed by chemical attack; a portion of the particle seems to have been partially exfoliated. In the montmorillonite product, Plate 1-C, the darker particles seen in the figure are thought to be undispersed montmorillonite particles or aggregates. Montmorillonite prepared for electron microscopy by the present method has this sort of appearance rather than the "fleecy cloud" morphology usually observed after dispersion in water.

Surface area measurements.-- The surface area of the calcium hydroxide employed in this study was measured by water vapor adsorption;

the value obtained was 36 $m^2/g$. The relatively coarse quartz used in this experiment had so small an area that it could not be measured by this technique. Thus, considering the proportions involved, the initial lime-quartz mixture had a surface area of not much more than 10 $m^2/g$. In contrast the surface area of the reacted mixture was measured as 53 $m^2/g$, a more than five-fold increase. Similarly the estimated surface area of the kaolinite-lime mixture before reaction was approximately 24 $m^2/g$; after the reaction the products yielded a value of 66 $m^2/g$.

Most of this increase in surface area is attributable to the formation of the calcium silicate hydrate products. Surface areas of CSH (I) phase materials are reported to range from about 135 to about 380 $m^2/g$ (Brunauer and Greenberg, 1962), and a similar range is reported for CSH(gel) materials.

There is a somewhat different situation with the montmorillonite material. The surface area of pure montmorillonite is about 800 $m^2/g$; that of the unreacted lime-montmorillonite mix would be of the order of 500 $m^2/g$. The measured surface area of the reaction product was 160 $m^2/g$. While this would not be an unreasonable value for a pure calcium silicate hydrate of the type generated, the present material contains a considerable content of unreacted montmorillonite. Seemingly, the residual montmorillonite does not contribute much to water vapor sorption, at least in the BET range of partial pressures. Sorption of water vapor on the internal portion of the montmorillonite surface cannot take place until the individual unit layers separate. It was thought pertinent to check on whether the residual montmorillonite present in the reacted product was free to undergo lattice expansion. Samples of the unreacted mixture and of the powdered reacted product

were treated with glycerol and examined by x-ray diffraction. The montmorillonite in the unreacted mixture expanded immediately, as expected, to yield a $d_{001}$ of 17.7A. No expansion was noted for the residual montmorillonite in the reaction product. Reexamination after a twenty-four-hour period of soaking in glycerol suggested that some expansion was taking place in the reacted mixture, but with apparent reluctance, considerable diffraction remaining at 12-13A. It appears that residual montmorillonite in the cemented material is prevented by some factor (perhaps mechanical) from undergoing the rapid lattice expansion usually associated with this phase.

Experiment 2 - Slurry Mixtures at 45°C

Physical appearance.-- Most of the samples were homogeneous slurries after the course of the reaction, but a large cemented mass of granular material was found in the montmorillonite reaction product, and the kaolinite product contained a substantial amount of small, hard granules dispersed throughout the slurry. Since considerable excess water was used, effective cementation had not been expected.

X-ray examination.-- Owing to the large excess of $Ca(OH)_2$ (to force the reaction toward completion with respect to the clay), initial x-ray examination yielded patterns dominated by residual $Ca(OH)_2$. Only slight carbonation seems to have occurred at this stage.

In order more closely to examine the reaction products, it was expedient to remove the excess lime by repeated dissolution in distilled water followed by centrifugation, the process being continued until the pH of the resulting suspensions was definitely below that

of a saturated $Ca(OH)_2$ solution (12.5). After this procedure the washed product was again examined in the wet state, then oven dried, powdered, and reexamined using the standard powder mount procedure. The dried powder was then used for DTA and electron microscopy.

The quartz reaction product, on initial examination, showed peaks for a calcium silicate hydrate product at 3.04A and 2.79A, a small broad peak at 8 A of unknown significance, and no evidence of carbonation. A powder mount of the washed and dried reaction product indicated some carbonation had taken place during processing, the broad peak at 3.04A having been sharpened, and a few weak calcite lines observed. There was broad general diffraction between 2.8 and 3.1A, suggesting that much of the calcium silicate hydrate reaction product formed was amorphous. The height of the residual quartz peak at 3.34 A was only 66 cps, compared to a height of several thousand cps for pure quartz under these conditions, suggesting that almost all of the quartz had been consumed in the reaction.

The hard granules in the kaolinite product were examined separately from the remainder of the slurry. The granules consisted of residual kaolinite and reaction products, but no free $Ca(OH)_2$, while the slurry consisted almost entirely of $Ca(OH)_2$, with a small content of the same reaction products, and no residual kaolinite. The reaction products were a poorly-crystalline calcium silicate hydrate phase and a hexagonal calcium aluminate hydrate phase with a 7.6A basal spacing. After the washing procedure the separate portions were recombined and a powder pattern was secured of the dried material. From this pattern it was clear that almost all the kaolinite had decomposed, the intensity of the 7.1A kaolinite peak being reduced

to 35 cps from an approximate value of 250 cps. The calcium aluminate hydrate formed was well crystallized over 20 reflections being attributable to this phase in the powder diagram. The 7.6A basal spacing was essentially constant in both the moist and dried conditions; this is not in accord with the variation in spacing reported by Roberts (1957) for the several hydration states of both $C_4AH_{13}$ and $C_2AH_8$. The pattern was similar but not identical to published diffraction patterns of $C_4AH_{13}$ (for example that of Buttler, Dent-Glasser and Taylor, 1959). It also closely resembled the powder pattern published by Hilt and Davidson (1961) for a well-crystallized lime-montmorillonite reaction product.

In the montmorillonite system it was also observed that the cemented portion was almost free of $Ca(OH)_2$, which was concentrated in the remaining slurry. The same reaction products were indicated, and in addition a broad peak at about 9A was observed initially, which was no longer present after washing and drying the material. Some residual montmorillonite remained, but it is difficult to assess the proportion. The peaks for the $C_4AH_{13}$-like product were much less intense in this product, which is to be expected in view of the lesser aluminum content of montmorillonite as compared to kaolinite.

Pyrophyllite was found in this experiment to react to a considerable extent, in contrast with the earlier result on this material. It may be that the finer particle size of the sample is responsible for the difference in behavior. The reaction products are similar to those for the montmorillonite and kaolinite, although the extent of the reaction was probably less.

The mica reacted extensively; the residual intensity of the 10A mica peak was only one-fourth as great as that of the original mica.

The same products were produced, a calcium silicate hydrate and a 7.6A compound resembling $C_4AH_{13}$. It was noteworthy that despite the considerable attack on the mica the remaining material retained all the lines characteristic of the $2M_1$ polymorph and these retained their original sharpness.

The illite reaction products can be described as similar to the mica products, and again, despite the substantial proportion of the illite that had reacted, the residual material was still well-crystallized and retained the lines characteristic of the $2M_1$ polymorph.

In contrast with the preceding results, it appeared that no reaction had taken place with the talc sample, except that some of the $Ca(OH)_2$ had carbonated. The residual talc lines were not appreciably weaker than those of the original sample, and no crystalline reaction products were found.

Differential thermal analysis.-- DTA patterns for five of the washed reaction products are given in Figure 3. Since the modified portable DTA unit was used, the peak temperatures are not directly comparable to those reported in the preceding experiment.

The patterns show a number of common features. All have relatively indistinct low-temperature dehydration endotherms, most showing an indication of several separate maxima in the range around 200°C. All show small endothermic responses at about 800°C, due either to carbonation or to the presence of a calcium silicate hydrate product, or both. The aluminosilicate products all show a small exotherm at about 900°C, the quartz product having a slightly more intense one at a somewhat lower temperature. These small exothermic responses are characteristic of the CSH(gel) phase.

Several points should be noted about the individual patterns. The quartz product gave no indication of the 573°C transition, testifying to the almost complete decomposition of the original quartz. A small endotherm in this pattern at 675°C is of unknown significance. The kaolinite product yielded an endothermic peak at 385°C, similar to that of the kaolinite reaction product of the first experiment, which was tentatively attributed to $C_3AH_6$, but that phase is not present here. The peak may be due to gibbsite, although no evidence of crystalline gibbsite was recorded in the x-ray results. The endotherm at 520°C in the present montmorillonite pattern seems to be the result of incomplete removal of unreacted $Ca(OH)_2$ in the washing procedure.

Electron microscopy.-- Representative electron micrographs of some of the reaction products are shown in Plate 2. In plate 2-A, the quartz product is fibrous, and closely resembles published electron micrographs of the CSH(gel) phase. A large, ragged particle in one corner of the figure is almost certainly a residual clay-sized quartz particle. The kaolinite product (Plate 2-B) is composed of individual fibrous particles of CSH(gel), thin sheets with crystalline outlines at least one of which is hexagonal (presumably the $C_4AH_{13}$ - like phase), and a few comparatively large particles with ragged edges, presumably residual kaolinite. The montmorillonite product (Plate 2-C) is more nondescript, but a considerable portion of the fine particles are fibrous in nature. The mica product (Plate 2-D) is distinctive. Although there are a few fibrous particles, almost all the material observable is of a unique ovoid or football-shaped morphology, not previously observed. Large, ragged mica flakes are

visible, some of which appear to have been delaminated as well as having suffered edge attack.

Experiment 3 - Dilute Suspension at 23°C

X-ray examination of this product disclosed that despite the long reaction period (6 months) considerable $Ca(OH)_2$ and kaolinite remained unreacted. The reaction products were the same as those encountered previously, a calcium silicate hydrate and the $C_4AH_{13}$-like phase with a 7.6A spacing. Little or no cementation occurred and the individual platy kaolinite and $C_4AH_{13}$-like particles were well oriented on the porous tile mount, with basal peaks many times stronger than those exhibited in random powder mounts. DTA of the material yielded separate and distinct low-temperature endotherms at 130°C and at 225°C; dehydroxylation endotherms for both $Ca(OH)_2$ and kaolinite, a small endotherm at 785°C, and a small but sharp a exotherm at 905°C. There was no endotherm at 385°C such as that observed in the corresponding product in Experiment 2, despite the fact that the crystalline components of the material revealed by x-ray diffraction were identical. Electron micrographs of the products revealed typical fibrous particles of CSH(gel), small, thin, but well-formed hexagonal plates attributed to the $C_4AH_{13}$-like phase, and large residual kaolinite particles marked by deformed and eroded edges.

## DISCUSSION

### Extent of Reaction

While no quantitative statement about the percentage of the silicate that has reacted in a given case is possible, it appears that reactions of $Ca(OH)_2$ with the various silicates has taken place

to an extent not previously reported. In certain instances, notably the reactions with clay-sized quartz, kaolinite, and montmorillonite in slurry mixtures it appears that by far the major part of the silicate has been destroyed and replaced by secondary calcium silicate hydrate and calcium aluminate hydrate compounds.

Mechanism of Reaction

Eades and Grim (1960) have suggested that the mode of reaction of lime is different with montmorillonite and other 3-layer clays than it is with kaolinite. They suggest that with the latter mineral the reaction seems to take place "by the lime eating into the kaolinite particles around the edges with a new phase forming around the core of kaolinite." The electron micrographs obtained in the present work appear to confirm the first part of this suggestion; it is obvious that the edges of the residual kaolinite particles are ragged and irregular as though they have been attacked chemically. Also, however, a certain amount of exfoliation seems to have taken place. However, the latter part of the quotation seems to imply an oriented transformation, which is difficult to envision in the light of the present results showing that at least two different reaction products are produced.

These authors also reported that for 3-layer clays "following the saturation of the interlayer positions with $Ca^{++}$, the whole clay mineral structure deteriorates without the formation of substantial new crystalline phases." The present evidence indicates a) that new crystalline phases are in fact produced by these clays, and b) that the residual portions of the 3-layer clays retain their crystallinity almost intact, even after most of the clay originally present has been

decomposed. The present results suggest that the decomposition of the 3-layer clays occurs from the edges of the particles in the same manner as it does with the kaolinites.

It appears to the present writers that the mode of chemical attack is largely through dissolution at the edges of the particles of the clay minerals and other silicates in the strongly basic environment characteristic of saturated $Ca(OH)_2$ solutions (pH 12.5), followed by precipitation of the calcium silicate hydrate and calcium aluminate hydrate phases.

Nature of the Reaction Products

It is felt that sufficient data have been obtained in this study to ascribe the reaction products to known phases. All the crystalline products are either calcium silicate hydrates or calcium aluminate hydrates. No known quaternary phase, as for example Strätling's compound, $C_2ASH_8$, was detected. This does not rule out the possibility of isomorphous substitution of silica for alumina or vice versa in some or all of the phases produced.

The poorly crystallized calcium silicate hydrates are not usually distinguishable from each other by x-ray diffraction; rather, observation of particle morphology and DTA patterns are essential to proper identification. Published results as reviewed by Taylor (1961) and by Brunauer and Greenberg (1962) and results by the present writers indicate that the following criteria are applicable:

CSH(I) - "foil-like", "snowflake" or very thin platy morphology, often crinkled or crumpled. DTA marked by strong, sharp exothermic response at 850-900°C.

CSH(II) - Morphology fibrous, sometimes as cigar-shaped bundles. DTA yields small exothermic bulge at about 400°C, and relatively small high-temperature exothermic peak at 850-900°C. X-ray pattern should yield diagnostic peak at 1.56Å.

CSH(gel) - Morphology fibrous, individual fibers appearing to consist of rolled-up sheets, often cemented laterally to form lathlike sheets. DTA yields weak exothermic peak at 850-900°C.

Application of these criteria suggest that the foil-like product formed with montmorillonite and kaolinite in Experiment 1 is CSH(I) and that the calcium silicate hydrate phase formed in all other experiments is CSH(gel), with the possible exception of the mica product of ovoid morphology. Thus, the same clay may produce different calcium silicate hydrates under different conditions.

Identification of the calcium aluminate hydrates depends more completely on x-ray evidence, since these phases are better crystallized. Identification of the $C_3AH_6$ in the kaolinite product of Experiment 1 is straightforward. The hexagonal calcium aluminate hydrate produced in other reaction products is apparently all the same phase, but the exact nature of this phase is open to some question. All these reaction products have $d_{001}$ spacings of close to 7.6A, regardless of the state of wetness or of oven-drying treatment. In contrast both $C_4AH_{13}$ and $C_2AH_8$ suffer successive decreases in spacing as they are dried (Roberts, 1957). Two phases are known that are similar to $C_4AH_{13}$ but contain $CO_3$--ions in certain lattice positions; hydrocalumite and calcium monocarboaluminate. The former phase is said to retain a $d_{001}$ spacing as high as 7.3A even after heating to 150°C, (Buttler, Dent-Glasser, and Taylor (1959). In contrast, the present reaction products, like $C_4AH_{13}$, decompose on heating to this temperature and produce a 6.1A spacing of much reduced intensity. The monocarboaluminate compound, containing a higher degree of $CO_3$-- substitution, exhibits a pronounced exothermic

response at about 550°C on DTA (Turriziani and Schippa, 1956); this is not observed on any of the present materials. Earlier work discussed a hexagonal compound of composition $C_3AH_{12}$ with an x-ray diagram similar to the present materials; but the existence of this phase has recently been discredited (Taylor, 1961; Jones, 1962). It appears likely to the present authors that the phase formed in these experiments is a $C_4AH_{13}$ stabilized to some extent by the occurrence of considerable isomorphous replacement of silica for alumina in the lattice. Such substitution would be difficult to prove in the present mixed materials, but was strongly indicated by the somewhat imperfect chemical analyses cited by Hilt and Davidson (1961) for mechanically-separated crystals of a lime-montmorillonite product that gave a similar x-ray pattern.

The montmorillonite-lime product of Experiment 1 was noteworthy in that no separate calcium aluminate hydrate phase could be detected. Thus, it seems reasonable to infer that the alumina released by $Ca(OH)_2$ attack on montmorillonite has been at least partially incorporated in the lattice of the CSH(I) phase produced. Isomorphous substitution of aluminum for silicon is of course widespread in clay mineral structures, and has been shown by Kalousek (1957) to occur in well-crystallized tobermorites.

Cementing Action and Strength Development

In prolonged soaking tests the cementation of the lime-kaolinite and lime-montmorillonite products of the first experiment (CSH(I)), were in no way inferior to that of the lime-quartz product (CSH(gel)). Thus, it is clear that the cementing action and consequent strength development is not an exclusive property of the latter phase among

calcium silicate hydrates. This tends to cast some doubt on theories of cementing action that depend on the particular fibrous or needle-like morphology of the CSH(gel) phase, such as those proposed by Bernal (1954), and by Brunauer (1962).

## CONCLUSIONS

These studies show that calcium hydroxide reacts at comparatively low temperature with clays, quartz, and other silicates to produce calcium silicate hydrates of high surface area referable to known tobermorite-like phases and generally also to produce well-crystallized calcium aluminate hydrates. Under appropriate conditions the reaction can lead to an almost complete decomposition of the silicate phase. Lime attack on quartz appears to produce CSH(gel) regardless of the experimental conditions; kaolinite and montmorillonite may yield either CSH(gel) or CSH(I). At slightly elevated temperatures $C_3AH_6$ may be produced; otherwise the alumina-bearing compound is usually a hexagonal phase similar to $C_4AH_{13}$ except that its basal spacing is maintained at approximately 7.6A regardless of the state of wetting or drying. No quaternary phases are formed. The mode of attack is postulated to involve dissolution at the edges of the silicate particles due to the high pH maintained by the calcium hydroxide, followed by precipitation of the reaction products. Under appropriate conditions CSH(I) of foil-shaped morphology has as high a degree of effectiveness as a cementing agent as does fibrous CSH(gel) produced under similar conditions.

## REFERENCES

Bernal, J. D. (1954) The structures of cement hydration compounds: in Proc. 3rd. Int. Symp. on Chem. of Cement, London, 1952, pp 216-236.

Brunauer, S., Emmett, P. H., and Teller, E. (1938) Adsorption of Gases in multimolecular layers: J. Amer. Chem. Soc., v. 60, pp 309-319.

Brunauer, S. (1962) Tobermorite gel- the heart of concrete: Amer. Scientist, v. 50, pp 210-229.

Brunauer, S. and Greenberg, S. A. (1962) The hydration of trialcium silicate and $\beta$-dicalcium silicate at room temperature: in Chemistry of Cement (Proc. 4th. Int. Symp., Washington, 1960), pp 135-165.

Buttler, F. G., Dent Glasser, L. S., and Taylor, H. F. W. (1959) Studies on $4CaO.Al_2O_3.13H_2O$ and the related natural mineral hydrocalumite.: J. Amer. Ceram. Soc., v. 42, pp 121-126.

Diamond, S. (1963) Tobermorite and tobermorite-like calcium silicate hydrates: their properties and relationships to clay minerals. Unpublished Ph. D. thesis, Purdue University, 262 pp.

Eades, J. L. and Grim, R. E. (1960) Reaction of hydrated lime with pure clay minerals in soil stabilization: Highway Research Board Bulletin 262 (N.A.S. - N.R. C. Publ. 771), pp 51-63.

Glenn, G. R. and Handy, R. L. (1963) Lime-clay mineral reaction products: Paper presented at 42nd Annual Meeting, Highway Research Board, Washington, D. C., 1963.

Hilt, G. H. and Davidson, D. T. (1961) Isolation and investigation of a lime-montmorillonite reaction product: Highway Research Board Bulletin 304 (N.A.S.-N.R.C. Publ. 932), pp 51-64.

Jones, F. E. (1962) Hydration of calcium aluminates and ferrites: in Chemistry of Cement (Proc. 4th Int. Symp., Washington, 1960), pp 205-246.

Kalousek, G. L. (1957) Crystal chemistry of the hydrous calcium silicates: I. Substitution of aluminum in the lattice of tobermorite: J. Amer. Ceram. Soc., v. 40, pp 74-80.

Kinter, E. B. and Diamond, S. (1955) A new method for preparation and treatment of oriented aggregate specimens of soil clays for x-ray diffraction analysis: Soil Science, v. 81, pp 111-120.

Majumdar, A. J. and Roy, R. (1956) The system $CaO-Al_2O_3-H_2O$: J. Amer. Ceram. Soc., v. 39, pp 434-442.

Mankin, C. J. and Dodd, C. G. (1963) Proposed reference illite from the Ouachita Mountains of southeastern Oklahoma: Clays and Clay Minerals, 10th Conf., Pergamon Press, New York, pp 372-379.

Roberts, M. H. (1957) New calcium aluminate hydrates: J. Applied Chem., pp 543-546.

Taylor, H. F. W. (1961) The chemistry of cement hydration: in Progress in Ceramic Science, V. 1, J. E. Burke, ed., Pergamon Press, New York, pp 89-145.

Turriziani, R. and Schippa, G. (1956) Concerning the existence of a hydrated calcium monocarboaluminate: Ricerca Scientifica, v. 26, pp 2792-2797 (in Italian).

White, J. L. (1956) Reactions of sodium salts with layer-lattice silicates: in Clays and Clay Minerals, Nat'l. Acad. Sci.-Nat'l. Res. Council pub. 456, pp 133-146.

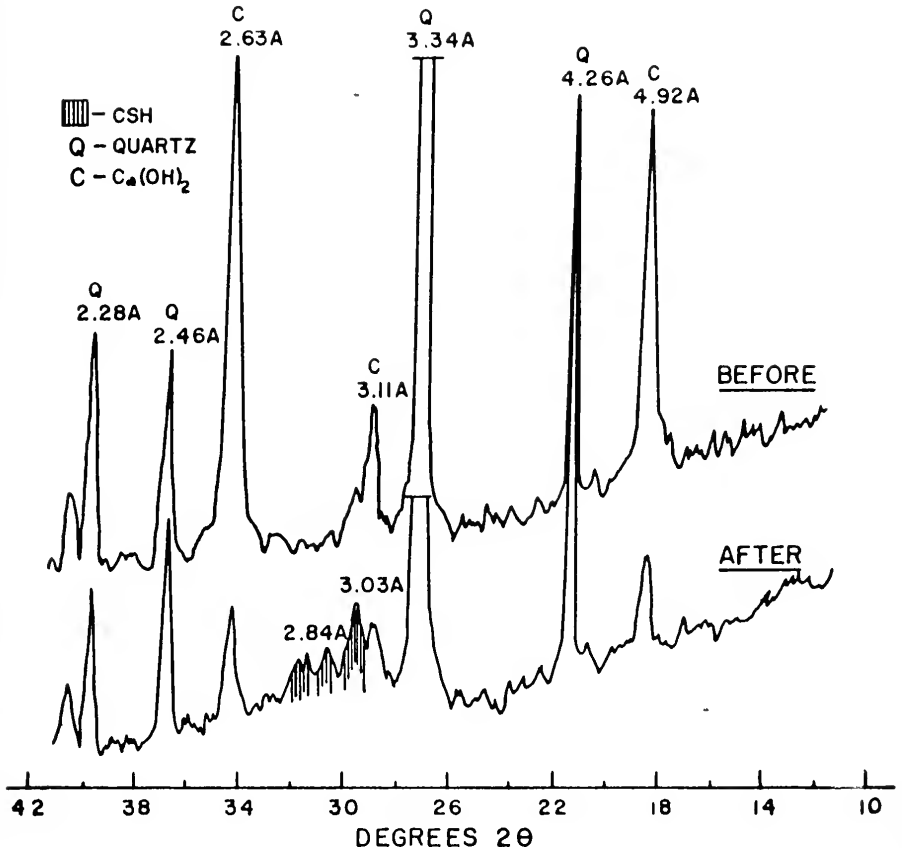



Figure 1-A. X-ray Diffractometer Traces of Quartz-$Ca(OH)_2$ Mixture Before and After Reaction at 60°C.

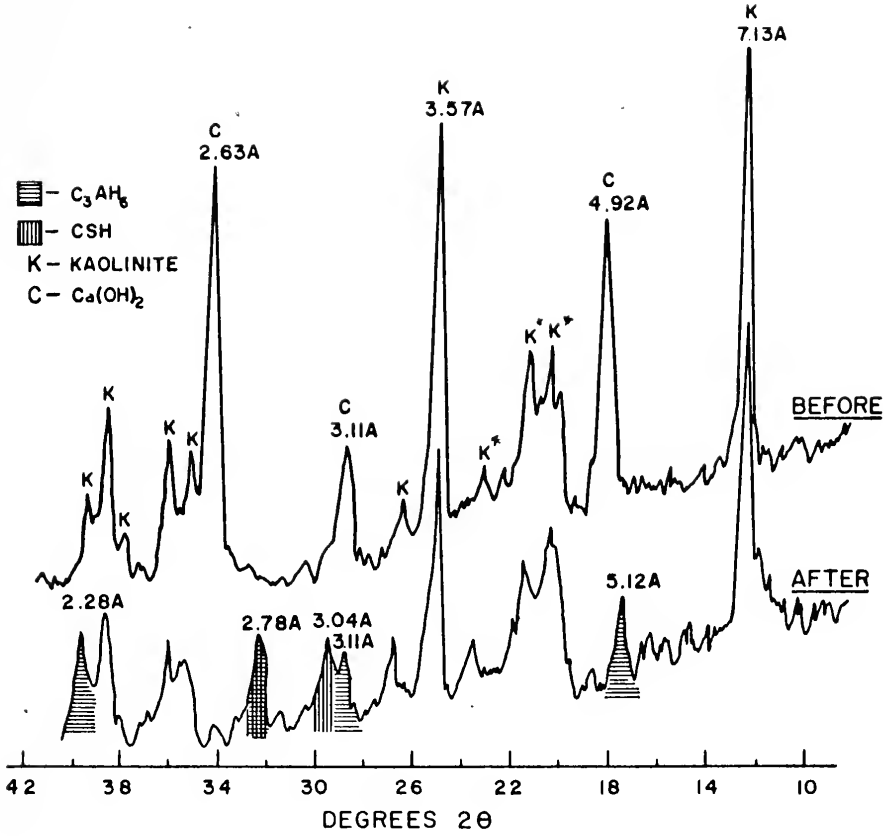



Figure 1-B. X-ray Diffractometer Traces of $Ca(OH)_2$-Kaolinite Mixture Before and After Reaction at 60°C.

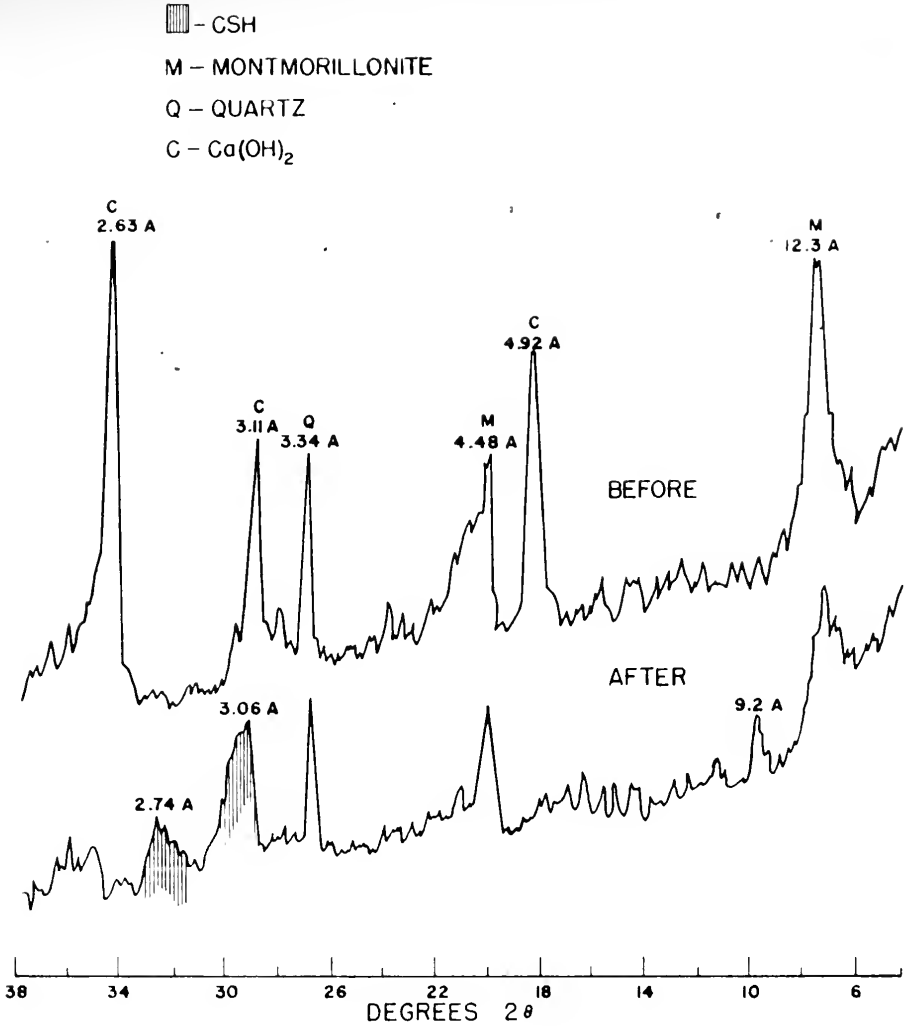



Figure 1-C. X-ray Diffractometer Traces of $Ca(OH)_2$ Montmorillonite Mixtures Before and After Reaction at 60°C.

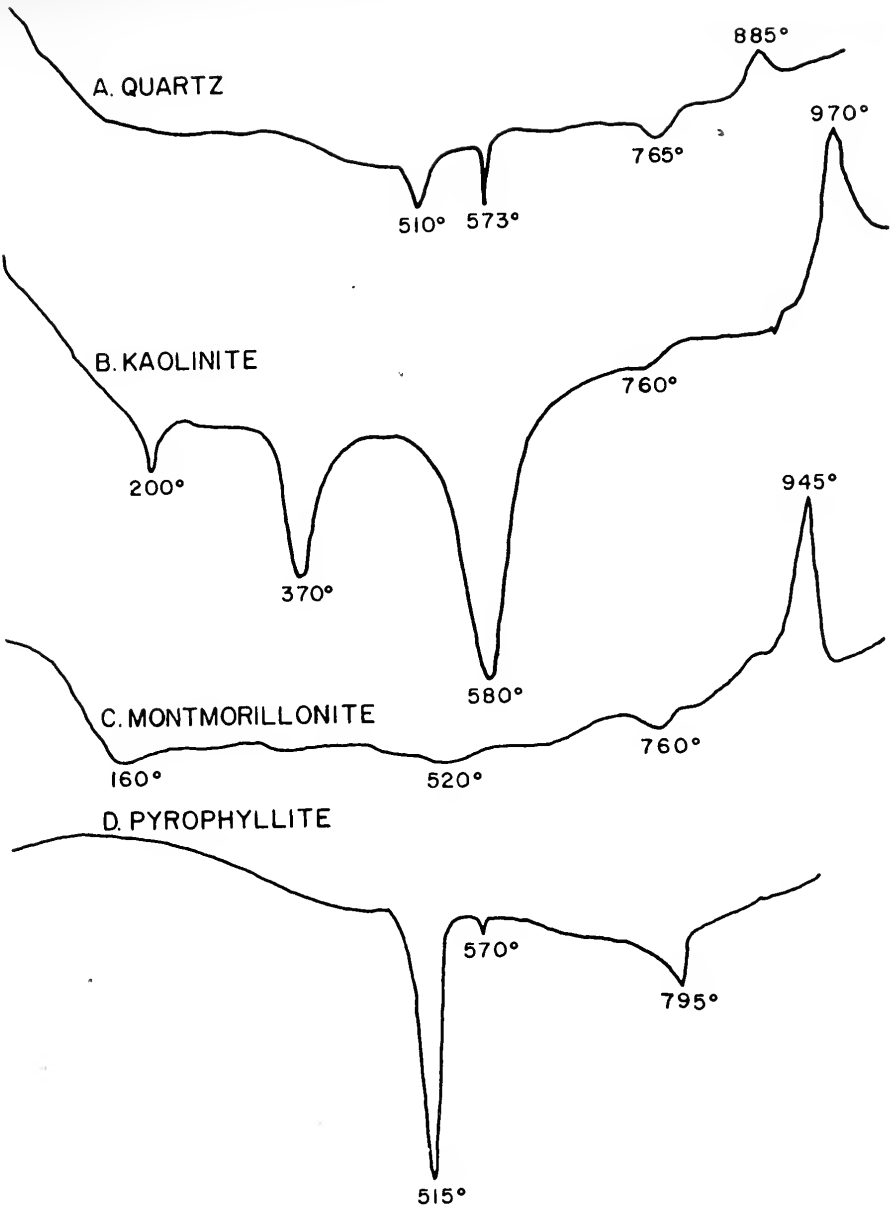



Figure 2. Differential Thermal Analysis of Products of $Ca(OH)_2$-Silicate Reactions at 60°C. Heating Rate 10°C Per Minute.

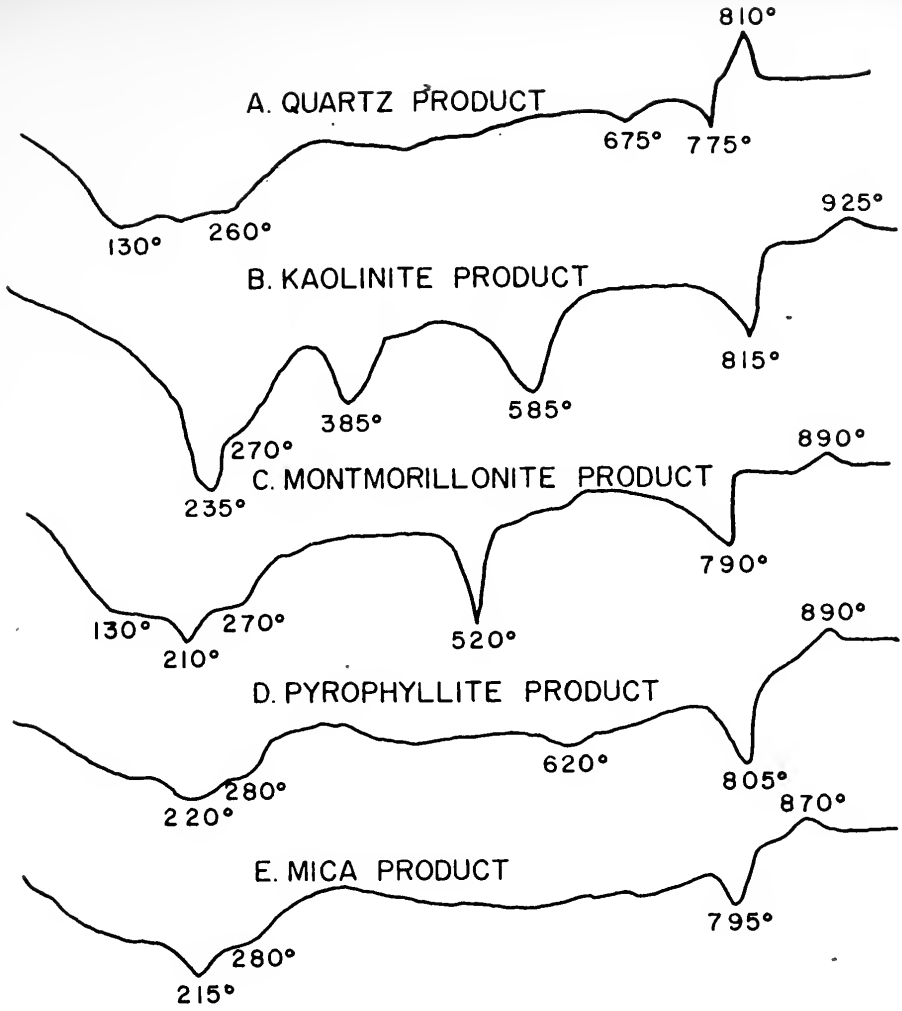
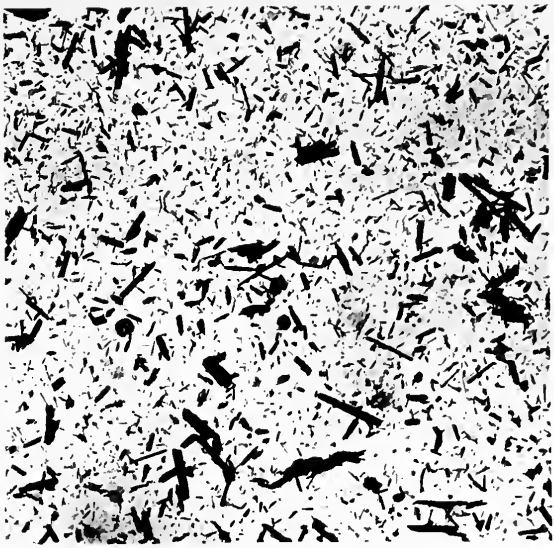



Figure 3. Differential Thermal Analysis of $Ca(OH)_2$-Silicate Reaction Products at 45°C. Heating Rate Varies from 58°C to 5° Per Minute.

(A)



(B)

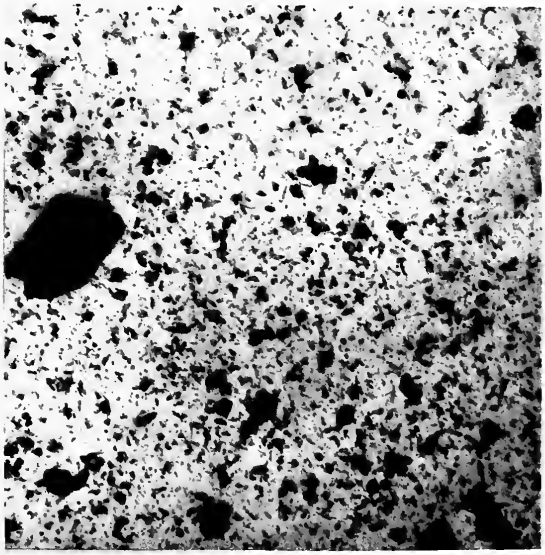


Plate 1. Electron Micrographs of $Ca(OH)_2$-Silicate Reaction Products at 60°C. (A) Quartz. (B) Kaolinite.

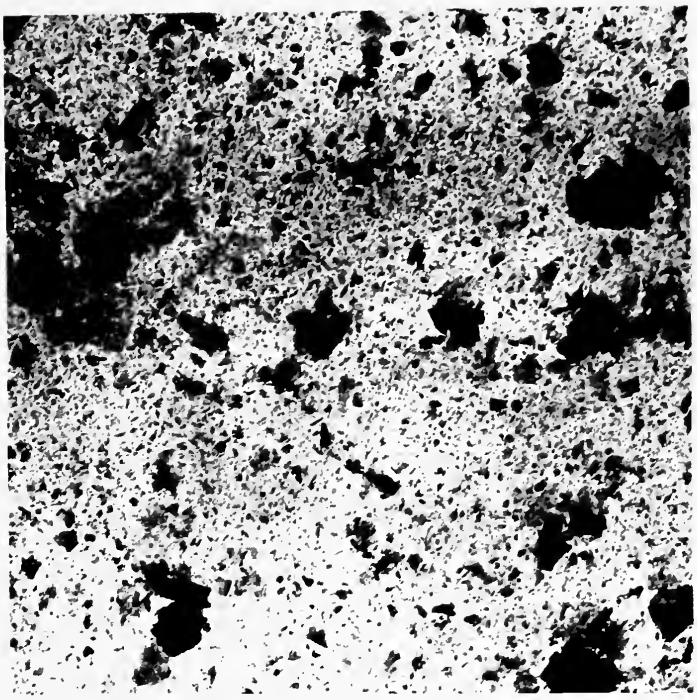


Plate 1-C. Electron Micrograph of $Ca(OH)_2$-Montmorillonite Reaction Product at 60°C.

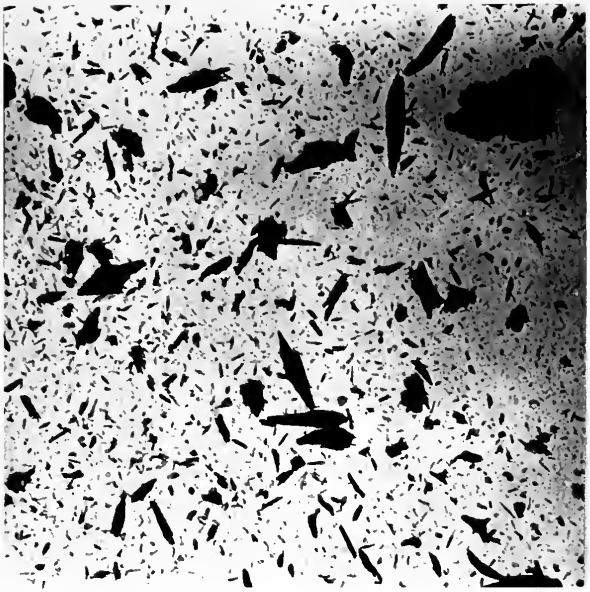
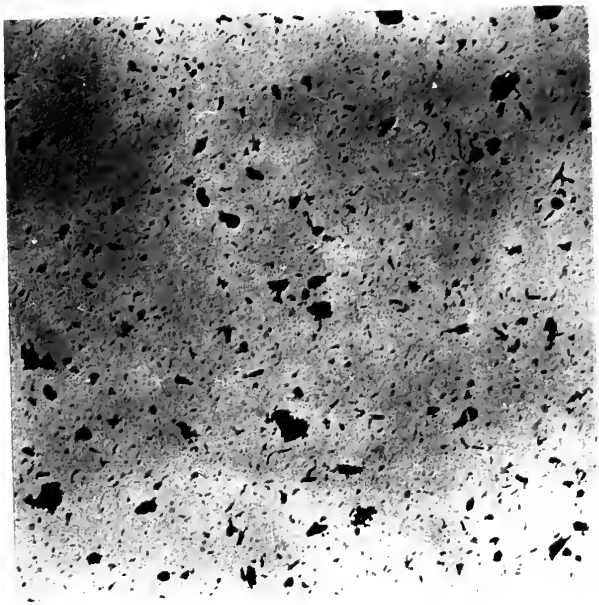


Plate 2-A. Electron Micrograph of $Ca(OH)_2$-Quartz Reaction Products at 45°C.

Plate 2-B. Electron Micrograph of $Cu(OH)_2$-Kaolinite Hydrothermal Products at 45°C.

C



D

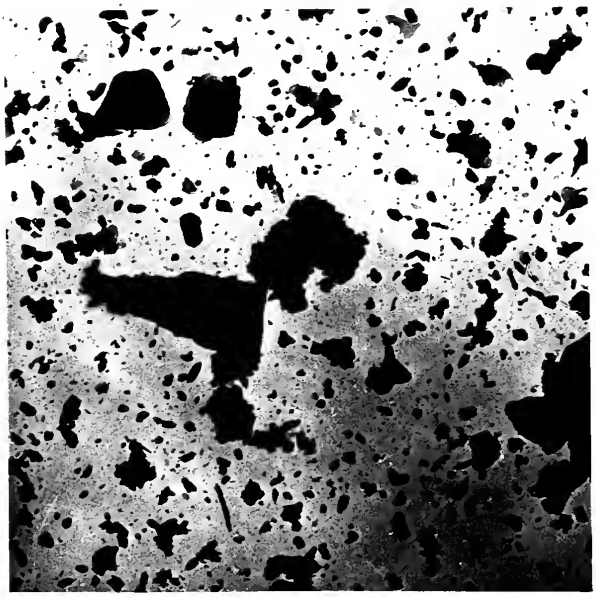


Plate 2. Electron Micrographs of $Ca(OH)_2$-Silicate Reaction Products at 45°C. (C) Montmorillonite. (D) Mica